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- (7) Applicant TEXACO DEVELOPMENT CORPORATION
  2000 Westohester Avenue
  White Plains New York 10650(U\$)
- Inventor: Alexander, David Christopher 4900 Black Angus Cove Austin Texas 78759(US) Inventor: Speranza, George Phillip 2800 Silverleaf Circle Austin Texas 78757(US)
- Propresentative: Harrison, Michael Robert et al Urquhart-Dykes & Lord 91 Wimpole Street London W1M 8AH(GB)
- (a) Novel bismeleimide derivatives.
- Novel bismaleimides of the formula

wherein n=1,2 or 3 are formed in two steps by reacting a diamine and maleic anhydride to form a bismaleic acid which is reacted with acetic anhydride in the presence of acetone to form the bismaleimide. This can then be further reacted with a high molecular weight polyoxyalkyleneamine resulting in a novel bismaleimide derivative of a higher molecular weight polyoxyalkyleneamine, which derivative has the general formula:

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wherein  $R^1$  and  $R^2$  are independently alkyl or hydrogen, x, y and z depend on the amine used, n is 1, 2 or 3 and m is predominantly 1.

#### NOVEL BISMALEIMIDE DERIVATIVES

This invention relates to bismaleimides. Mure particularly, this invention relates to novel bismaleimide derivatives obtained from oxyethylene diamines and anhydrides or higher molecular weight polyoxyalkylene amines.

Bismaleimida polymers are important primarily for their thermal stability, which usually results from aromaticity in the structure. Although the majority of bismaleimidos have therefore been prepared from aromatic diamines, allphatic compounds can also provide benefits in improved processibility, flexibility and solubility. Bismaleimides have, for example, been prepared from alkylene-diamines (J. Appl. Poly. Sci., 29, 891-899 (1984) and from JEFFAMINE® ED-diamines (U.S. Patent 3,951,502). In a scried of Japanese patents issued to Mitsui Thatsu Chemicals (JP 82 205,413; 83 40,374; 83 15,515; 83 136,637), bismaleimides were also prepared from diamines such as 4,7-dioxadecane-1,10-diamine (reduction product of cyanoethylated ethylene glycol) and rolated diamines, these are used with polybutadiene in preparation of copolymers. The maleimide of triethylene glycol monoamine is also reported in one of these patents. Use of the oxyethylene group to increase flexibility has been effective in some other types of polymers as well. In J. Macromol. Sci.—Chem., A21, 1117-1135 (1984) there is described preparation of "reactive plasticizers" with acetylene endgroups and internal oxyethylene groups. Stenzenberger, in German Patent No. 2,127,024 disclosed the preparation of an aliphatic bismaleimide from 2,2,4-trimethyltrexane-1,6-diamine and in German Patent No. 2,105,974 he described its thermal polymerization.

The use of mixtures of polyoxyalkylene bismaloimides (with molecular weights greater than 400) and aromatic bismaleimides in preparation of flexibilized polybismaleimides is disclosed by de Koning in European Patent Application No. 206,383. While the heat distortion temperature tell with increasing amounts of flexibilizing bismaleimide, the elongation and flexure at break both increased.

In IJ S. Patent No. 4,237,262, Jones discloses a low temperature curable composition comprising at least one curable polyimide prepolymer formed by heating an aliphatic expelliplene bismalelmide with an aromatic polyamine and at least one aromatic bismalelmide and at least one aliphatic epoxy resin. The reaction product provides at least two functional epoxy groups to provide a low temperature curable composition. In U.S. Patent No. 3,951,902 Junes et al. disclose a compliant polyimide having superior thermal mechanical properties produced by reacting an aromatic bis(furfurylimide) with an aliphatic ether bis(materinide) via a Diels-Alder reaction.

In U. S. Patent No. 4.116.937. Jones also disclosed a rosin system prepared by Michael addition of a mixture of oxyalkylene and aromatic bismatelmides to aromatic diamines. The oxyalkylene bismatelmides have molecular weights of about 750, and the product is a glassy solid at room temperature.

In the work described in 4.116,937 the objective was to make elastomers. The elongations for the polymers described in the examples therein range from 70% to 170%. These polymers were probably not very rigid, this property being a function of the molecular weight of the amines used and the distance between maleimide units. Another disadvantage is that the amines used here are aromatic amines, which are in many cases known or suspected to be carcinogenic or otherwise toxic; although the issue is not specifically addressed, it is not likely the "flexible polylmide precursor", with its aromatic content, would be soluble to any great extent in water.

Nagocaki, in European Patent Application 191,931, reveals the use of certain oxyalkylene bismalcimides in rupper compositions.

A curable resin composition is disclosed in Jpn. Kokal Tokkyo Koho JP 58, 136,637 [83,136,637] 13 Aug. 1983 to Mitsui Toatsu Chemicals. The compounds contains an alliphatic imide and polybutarliene containing double bonds.

A Japanese Patent to Mitcui Tontau Chemicals, Inc. (JP 58,127,735 [83,127,735] (Cl. CORG 73/10), 29 Jul. 1983) discloses neat resistant electrical insulators for printed circuit boards which are prepared from mixtures of aliphatic polyether bisimides, aromatic bisimides and diamines.

An arucle by White in Ind. Eng. Chem. Prod. Res. Dev. 26, 395-400 discusses the fact that bisimides offer potential for the synthesis of high-molecular-weight, step growth polymers. It is stated they are flanked by two electron-withdrawing carbonyl groups, and the electrophilic maleinulde carbon-carbon-double bond is especially labile to nucleuphilic attack and yields Michael type adducts with both amines and thiols. The paper finances on the requirements for preparation of these polymeric Michael adducts, with additional emphasis on the effects of the enormous structural variety available within the class in the thermat and physical properties of those new resins.

In the art experimental data are available wherein polymers were synthesized which are structurally

related to those formed by nuclcophilic or Michael addition of diaminoarenes, but which had more flexible backbones and lower glass transition temperature (Tg). See "Reaction of Diaminoalkanes with Bismalcimides: Synthesis of Some Unusual Polyimides", Journal of Applied Polymer Science, Vol. 29, 891-899 (1984).

Shaw and Kinloch have studied the effects of rubber concentration on the morphology, bulk mechanical and thermal properties and the adhesive strength of the bismalefmide by the addition of various amounts of a carponyl-terminated butadiene (CTBN) rubber toughening agent, and concluded that surprisingly large amounts of CTBN rubber can be added to substantially improve the fracture resistance of the bismalefmide resin without sacrificing other important properties. (see "Toughened Bismalefmide Adhesives". Int.,I Adhesion, July 1985, pp. 123-127.)

A growing number of applications for polyimides are discussed in an article titled "Ptemium Performance from Polyimides" in ME, January 1986, p. 14-19.

In U.S. Patent No. 4,277,502 Mueller discluses water-insoluble hydrophilic copolymers consisting of a hydrophilic polymer of monoplefinic monomers cross-linked with a major amount of a diolefinic non-hydrophilic macromer.

Polymerization of the hismaleimide of dimer diamine, which also contains a hydrocarbon backbone. Is disclosed in U.S. Patent No. 4,564,663. The product polymer is hard and thermally stable.

It appears there is a large market for bismalelimides and a good deat of research in the art has been directed toward studying properties of and better methods for producing these compounds. Bismalelimide compounds are increasingly important in high performance polymers commonly used as matrix resin for composites. It is believed that the polybismalelimide derivatives of the instant invention, particularly those derived from distriction and total the polybismalelimide including bisaminoethyl ether. JEFFAMINE® EDR-148 and JEFFAMINE® EDR-192 would be useful as monomers in homopolymers and copulymers and would exhibit advantages including improved flexibility, processibility, toughness and solitibility. They could be used alone or in combination with other materials such as aliphetic or aromatic diamines or unsaturated compounds (including aromatic bismalelimides) to give copolymers. Additionally, the polybismalelimide derivatives from higher weight polyoxyalkylene aminos have the advantage that aromatic amines, which are in many cases known or suspected to be carcinogenic or otherwise toxic, are not used to prepare the materials.

In another embodiment of the invention monomers are prepared from higher weight polyoxyal-kyleneamines having a polyoxyalkylono backbone and aromatic bismalelmide termination.

The products resulting from the latter embodiment would be of particular interest because they are formed from the reaction of two commercially available inaterials. The method of preparation disclosed is much easier than the direct route, using malain anhydride. These materials are useful in the preparation of homopolymers and copolymers that may be suitable as matrix resins in composites.

The series of oxyethylene diamines consisting of BAEE (bipaminoethyl ether, or diethylene glycol diamine), JEFFAMINE® EDR-148 (triethylene glycol diamine), and JEFFAMINE® FDR-192 (tetraethylone glycol diamine) are promising candidates for conversion to bipamaleimides (eqs. 1.2). Incorporation of bipamaleimides made from these diamines could give new prepolymers and polymers with chhanced flexibility, processibility or solubility. The polymor prepared from the adduct of EDR-148 and EDR-148 BMI was a relatively hard material with a high flexural modulus (close to 500,000 psi). In the instant invention there was less distance between the maleimide units than in, for example, the case of 4.116.937, where the amines had a minimum molecular weight of 600, and therefore the instant polymers exhibited more rigidity. Another advantage of the instant invention is that the prepolymer products exhibit solubility in water, unlike products resulting from the use of aromatic amines.

One derivative, in particular, is the bismalelmide of triethylene glycol diamine. This bismalelmide chould be quite useful as a monomer, but it is solid. This detracts from the usefulness for many applications. By a method disclosed in another embodiment of the instant invention it is converted to a liquid form suitable for polymerization. Water-soluble bismalelmides and polybismalelmides have been sought in recent years, and compounds such as the prepolymers of this invention could prove to be especially useful in this respect.

In accordance with the present invention there is provided a novel bismaleimide derivative which is of the formula A or B and is formed at a temperature sufficient to cause thermal reaction between heated components of the mixture of:

(a) at least one diamine of the formula

NzNCI IzCHz-(-OCHzCHz-)n-NHz

wherein n equals 2, 3 or 4 and

(b) maleic anhydride

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wherein components (a) and (b) form a bismalearnic acld represented by the formula

which is further reacted with acetic anhydride to form a bismaleimide of the formula A;

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wherein n = 2, 3 or 4, which optionally can be further reacted with a polyoxyalkyleneamine with a molecular weight greater than about 200 resulting in a bismalelmide derivative of a higher molecular weight polyoxyalkyleneamine of formula B:

wherein  $R^1$  and  $R^2$  are independently alkyl or hydrogen, x, y and z depend on the amine used, n is 1, 2, or 3, and m is predominantly 1.

The exyethylene bismateimide derivatives are prepared from an exyethylene diamine having the formula:

 $H_2NGH_2GH_2-(-OCH_2GH_2-)_n-NH_2$  (I) where n=2,3 or 4 which is combined with maleic anhydride of the formula:

to form a bismaleamic acid of the formula:

which is reacted with acetic anhydride in the presence of acetone solution to form a bismaleimide of the formula:

where n = 2, 3 or 4.

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The novel bismalcimide derivatives of higher molecular weight polyoxyalkyleneamines represented by the formula:

use formed by combining I and II to form III and IV which is then further reacted with a polyoxyalkyleneamlne with a molecular weight greater than about 200 to form the above.

In another embodiment aromatic bismaleimide derivatives are prepared by reaction of polyoxyal-kyleneamines with commercially available aromatic bismaleimides. These materials are useful in the preparation of homopolymers and copolymers that may be suitable as matrix results in composites. This can be represented by the following:

$$\begin{array}{c|c} & & & \\ & & \\ & & & \\ & & \\ & & \\ & & & \\ & & \\ & & & \\ & & \\ & & \\ & & & \\ & & \\ & & & \\ & &$$

where  $R^{n}$  and  $R^{n}$  are independently alkyl or hydrogen, x, y, and z depend on the amine used, n is 1, 2, or 3, and m is predominantly 1.

Preparation of monomers containing polyoxyelkylene backbones and aromatic bismaleimide termination in this become embodiment is much easier than by direct route (roaction of the pulyoxyalkyleneamine with maleic anhydride); from monomers bismaleimide copolymers and homopolymers may be prepared by several methods.

## Diamine Starting Materials

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The expethylene diamine reactants represented by (1) above include di-, tri-, and tetraethylene glycol diamine compounds.

Of special note are the ".IFFFAMINE"® EDR scries diamines". The structure of "JEFFAMINE® EDR" can be generically illustrated as follows:

H2NfCH2CH2O},CH2CH2NH2

where n = 2, 3.

In one example the diamine used is JEFFAMINE® EDR-148. JEFFAMINE® EDR-148 is the trademark for a triethylene glycol diamine produced by Texaco Inc. In another example the diamine is JEFFAMINE® EDR-192 is the trademark for tetraethylene glycol diamine produced by Toxaco.

Preparation of the bismaleimides is effected by reacting a diamine with 2 moles of maleic anhydride. These reactants are mixed with a small amount of solvent to facilitate the mixing process and the solvent is subsequently driven off after the bismaleimide is formed.

## Preparation of the Bismaleimides

The bismalelmide product is preferentially formed when a bis(amic acid) (prepared from the oxyethylene diamines and maleic anhydride) is reacted with an excess of anhydride at autogenous pressure at a temperature within the range of about 50°C on about 150°C for a reaction time within the range of about 0.5 to about 12 hours. Good results are obtained by heating the mixture at 60° to 100°C for 0.5 to 4 hours to provide complete reaction of the diamine and the anhydride. Normally, the reaction will to to completion after a reaction time within the range of about 1-2 hours.

The reaction is complete when essentially all of the diamine has reacted with the maleic anhydride. Under the noncatalytic reaction conditions employed herein, the amine groups of the polyoxyalkylene diamine are essentially unreactive with each other.

The bismalcimide monomers and prepolymers that are formed by the process of the present invention are liquid or crystalline solid materials having a molecular weight within the range of about 250 to about 1000 or to about 0000 in the case of the higher molecular weight derivatives containing no terminal primary amine groups.

The reaction mixture will comprise a diamine addition product which may be generally characterised by the following formula:

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wherein n represents 1, 2, 3 or 4.

A veriety of molecular configurations is possible for the bismaleimides of the present Invention, depending on the starting materials. For example, where the starting materials are bisaminoethyl ether and maleic anhydride, the bismaleimide will have the formula:

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The bismaleimide derivatives of higher molecular weight polyoxyalkyleneamines are formed by reacting the bismaleimide formed by the process described above with high molecular weight polyoxyalkylene amines described below.

Where JEFFAMINE® EUH-192 is reacted with maleic anhydride, the reaction product that is formed will be composed principally of a bismaleimide addition product having the formula:

In another embodiment of this invention the solid bismaleimides of this invention are converted to liquid prepalymers.

The significance of this invention is that the bismaleimide of triethylene glycol diamine or other solid oxyethylene bismaleimide should be quite useful as a monomer except that it is a solid, which detracts from its utility for many applications. By conversion into the prepolymer the oxyethylene bismaleimide is unexpectedly converted into a liquid form suitable for polymerization. The liquid products can be cured thermally to give hard polymers. The polymers are potentially useful as matrix resins or components theroof containing ether linkages that may impart improved processibility.

The liquid form is obtained from the bismaletmide by reacting the solid with EDR-148 to give a liquid bismaleimidoaspartimide prepolymer. In many applications liquids are preferable to solids and the liquid prepolymers can be cured thermally.

This can be represented by equation 3:

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where m=2, n=2 and k is predominantly 1.

# Examples For The Proparation of Diamine Dismaleimides From Oxyethylene and Anhydrida

The preparation of the prepolymer is carried out at temperatures up to 125°C and polymerization is carried out at subatmospheric or superatmospheric pressures.

In Specific Examples I to VI the preparations of three hismaleamic acids were quite similar and were based on the preparations of bismaloimides from alkylone-diamines reported by White (J. Appl. Poly. Sci 29, 891-899 (1984), incorporated herein by reference.

Specific Example VII demonstrates the preparation of the bismaleimideaspartimide

Specific Example VIII demonstrates the use of the bismaleimideaspartimide in polymer preparation.

The following examples are given in the way of illustration only and are not intended as limitations on the scope of the invention.

# SPECIFIC EXAMPLE I

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In the preparation of the bismaleamic acid from triethylene glycol diamine, maleic anhydride (62 g, 030 mmol) was dissolved in 250 michloroform; the polution was cooled to 8°C in 500 mi,3-necked round-bottomed flask equipped with magnetic stirrer and nitrogen inlet. Triethylene glycol diamine (40 g, 320 mmol) was added dropwise (with the temporature kept below about 10°C) over a period of three hours, which led to precipitation of a white solid within the first hour. After the addition was complete, the sturry was allowed to warm to room temporature and stirred for two neurs more. The mixture was then filtered: after it was dried under vacuum a white powder (105 g, 95%) was obtained, m. p. 100-151.5°C. Titration of this colid chowed an acid content of 5.77 meg/g; theoretical acid content is 5.78 meg/g. Spectra (nmr, ir) were consistent with the assigned structure.

# SPECIFIC EXAMPLE II

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Preparation of the tetraethylene glycol diamine maleanic acid was carried out similarly, but this material did not precipitate as a solid. Near the end of the addition two phases appeared; the upper phase was a chloroform solution of the bicmaloamic acid. After removal ut the chloroform the residual oil solidified and gave, after drying under vacuum, a white powder (53 g, 87%), m. p. 96-101 °C. Titration of this solid yave an acid content of 5.24 mog/g; theoretical acid content is 5.15 meg/g. Spectra (nmr, ir) were consistent with the assigned structure.

### SPECIFIC EXAMPLE III

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The bismaleamic acid from diethylono glycol diamine precipitated immediately on addition of the amine to the anhydride solution and was isolated as a white powder. After it was dried under vacuum 60.3 g (96%) was obtained, m. p. 164-166° C. The acid content was found by titration to be 5.73 meg/g; the theoretical acid content is 6.67 meg/g. Spectra (nmr. ir) were consistent with the assigned structure.

## SPECIFIC EXAMPLES IV-VI

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Examples IV through VI represent the accound step of the two-step process wherein the bismaleimides are prepared from the bismaleamic acids.

The bismaleimidos were prepared by reaction of the bismaleamic acid with acetic anhydride in acetone solution in the presence of triethylamine and acetate salts.

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#### SPECIFIC EXAMPLE IV

In the preparation of triethylene glycol diamine bismaleimide, the bismaleamic cold (00 g, 0.17 mol), triethylamine (11.5 g, 0.11 mol), and sodium acetate trihydrate (1.9 g, 0.13 mol)) were added to acetono (200 ml) in a 1000 ml 3-necked round bottomed tlask fitted with nitrogen inlot and magnetic stirrer, Acetic anhydride (110 g, 1.08 mol) was added, and the resulting mixture was heated at reflux (70°) for 2.5 hours; during this period the solid dissolved and the solidion darkened. About 00 ml acetone were then distilled. The residue was allowed to cool to 50°, and must of the rest of the anetone was removed under vacuum with the temperature kept below 60°. Some solid appeared in the dark residue, and the resulting paste was poured into 500 ml stirred distilled water. A precipitate formed and was filtered from the dark solution, then washed on the filter with methanol (3 x 40 ml) and dried under vacuum to give 20 g (37%) off-white powder, m. p. 92-90°. Specua (mm, lr) were consistent with the assigned structure.

#### SPECIFIC EXAMPLE V

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When tetraethylene glycol diamine (JEFFAMINE® CDR-192) was the bismaleamic acid precursor, a colid bismaleimide could not be prepared. Instead, a dark, viscous liquid formed which was more soluble than the other two products and could not be induced to solidity. The proton nmr.spectrum of this material appeared to be that of a mixture containing a major amount (ca. 70% by nmr) of the desired bismaleimide along with smaller portions of unidentified impurities.

#### SPECIFIC EXAMPLE VI

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Proporation of the bismaleimide from diethylene glycol diamine was carried out identically and afforded a very light tan solid, m.n. 154.5-156.5°. Spectra (nmr, ir) were consistent with the assigned structure.

Heating of these distrialelmides alone at 180°-200° for 0.5-1.0 hours gave hard, transparent, somewhat brittle brown polymers with decomposition temperatures found by thermogravimetric analysis to be approximately 440° C (bisaminoethyl ether derivative) and 400° C (biothylene glycol diamine derivative).

#### SPECIFIC EXAMPLE VII

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Example VII demonstrates the preparation of the bismeleimide-spartimide from the triethylene glycol bismeleimide. In a 250 ml 3-necked round-bottomed flask, under nitrogen, a solution of triethylene glycol diamine (1.68g, 11.3 mmol) in 10 ml chloroform is added dropwise to a solution of triethylene glycol bismeleimide (7.00g, 22.7 inmol) in 40 ml chloroform at 40. The resulting orange solution is heated at reflux for 1.5 hours and then concentrated under vacuum to give immediately 8.1g of the prepolymer as a viscous orange liquid.

### SPECIFIC EXAMPLE VIII

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Example VIII demonstrates the use of the bismaleimides partimide in polymer preparation. A 17.5g sample of the prepolymer was heated at 60° under vacuum for 3 hours, then poured into a 5" x 3.25" mold which was placed into an even at 125°. The even was heated to 155° over a one hour period and then held at 165-175° for an additional two hours. The product polymer was obtained as a hard, red, fairly stiff plaque with a room temperature floxural modulus (ASTM D-790) of 460,000 psl.

Other examples include bismaleimides of 2,4-toluenediamine, 4,4 -diaminodiphenylmethane, 1.4-diaminobenzene and 1,3-diaminobenzene.

One aromatic bismaleimide which works well in 4,4'-bismaleimidudlphenylmethane (MDARMI), shown below:

# Examples for the Preparation of the Bismalelmide Derivatives of Higher Molecular Weight Polyoxyalkyleneamines

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The movel uismalelmides are prepared by reacting low molecular weight oxyothylonediamines with higher molecular weight polyoxyalkyloneamines to form bis (malelmideaspartimide) compounds. As mentioned the reaction is a Michael addition. The reaction works particularly well with propylene oxide capped polyoxyalkyloneamines. The low molecular weight bismalelmides react with the propylene oxide capped glamines in a 2/1 ration to give bis-Michael adducts.

In the mothod of the instant invention the bismalelmide is dissolved in chloroform and the polyoxyal-kyleneamine is gradually added. The resulting solution is stirred at a temperature of from 20°C to 140°C with the preferred range being 40-80°C for a period of from 1 to 4 hours. The chloroform is then removed under vacuum with the temperature kept below 56°C. In most cases the product is a liquid at room temperature.

In the method of this invention, the proceuro may range from 0.5 alin to 50 atm. The preferred pressure is almospheric.

The Polyoxyalkyleneamines used for the preparation of derivatives with higher molecular weight.

Generally, polyoxyalkyleneamines which will work are those with a molecular weight of greater than 200.

One group of suitable amines are pulyoxyalkylenediamines of the formula: NH<sub>2</sub>CH(CH<sub>3</sub>)CH<sub>2</sub>-(OCH<sub>2</sub>CH(CH<sub>3</sub>)]<sub>x</sub>-NH<sub>3</sub>

Compounds having the above formula include JEFFAMINE® D series diamines which are based on a polypropylene glycol (PPG) backbone and are available in a variety of molecular weights. They are low viscosity, light-colored liquids exhibiting low vapor pressure and high primary content. D-corlos emines include D-230, D-400 and D-2000 with approximate molecular weights of 230, 400 and 2000 respectively. Good results were obtained using D-400 as demonstrated in Specific EXAMPLE I.

Another group which can be used is water-soluble diarnines based on a predominantly polyethylene glycol (PEG) backbone of the formula:

NH2CH(CH3)CH2-{OCH(CH3)CH2}-{OCI12CH2}-(OCH2CH(CH3)]-NH2

Polyoxyethylenediamines having this formula include the JEFFAMINE®-CD series diamlnes. ED series include ED-600, ED-900 and ED-2000, having approximate molecular weights of 600, 900 and 2000 respectively.

## Aromatic Bismalelmides

Where aromatic bismaleimide derivatives of polyoxyalkyleneamines are the desired product suitable aromatic bismaleimides can be selected from among those which are commercially available.

One suitable aromatic bismaleimide has the formula:

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Preparation of the aromatic bismaleimide derivatives should be carried out under a temperature of from 46°C to 75°C. The preferred temperature is under approximately 126°C.

The products resulting from this method are used to make polymers by reaching them at a temperature of at least 150°C for about 30 minutes to 2 hours in the prosence of either an additional amount of the higher molecular weight bismoleimide derivative or in the presence of a suitable copolymer.

The following examples are given in the way of illustration only and are not intended as limitations on the scope of the invention.

Examples I through IV demonstrate the proporation of bismalelmide derivatives of higher molecular weight polyoxyalkyleneamines.

In these preparations the diamine (next or in chloroform solution) is added to a chloroform solution of the oxyethylene bismalelmide. The following illustrates the procedure for two different potyoxyal-kyleneamines.

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## SPECIFIC EXAMPLE I

The bismaloimide of bisantinoethyl ether (24.5g, 93 mmol) was dissolved in 175 ml chloroform at 55°C in a 500 ml 3-necked round hottom flask; the D-400 (18.6g, 48 mmol) was added over a 10 minute period. The resulting solution was listated at 55°C for an hour and then allowed to bit at room temperature overnight. The chloroform was removed under vacuum, with the temperature kept below 55°C, leaving a tan paste, 47g, 110% (chloroform not entirely removed. The nmr analysis of this material was as expected for the desired product.

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# SPECIFIC EXAMPLE II

The bismaleimide of JEFFAMINE® EDR-148 (triethylene glycol diamine) 14.1g, 45.6 mmol) was dissolved in 100 ml chloroform in a 250 ml 3-necked round-bottomed flask. The ED-900 (20.0g. 22.2 mmol) was added in a steady stream, and the resulting orange solution was heated at 65°C for 2.5 hours. The chloroform was then removed under vacuum, with the temperature kept below 55°C, giving a viceous, rather turbid brown liquid, 33.1g, 97%. The proton nmr spectrum of thic motorial was as expected for the desired product.

Use of these products in preparation of polymers, both alone and with other bismalelmides, is illustrated in the following examples:

### SPECIFIC EXAMPLE III

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The product of Example II above (1.0g) was heated with the blomaloimide of JEFFAMINE® EDR-148 (1.0g) at 185°C for 45 min. The product was a clear, hard, dark orange polymer with a decomposition temperature of 380°C determined by tga in nitrogen.

# SPECIFIC EXAMPLE IV

The product from Example I shave (2.6g) was heated at 180°C (after a brief initial heating to 215°C) for one hour. The product was a clear, flexible, orange polymer with a decomposition temperature of 270°C determined by top in nitrogen.

Examples V through IX demonstrate the method of producing an aromatic bismalelmide derivative and significant the use of the products in homopolymerization and copolymerization. In a general preparation of the compounds of this invention, a chloroform solution of the polyoxyalkylene diamine is added to a chloroform solution of the aromatic bismalelmide. The resulting solution is optionally heated and then concentrated under vacuum to afford the bismalelmide product, which can be polymerized.

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## SPECIFIC EXAMPLE V

# 15 Reaction of JEFFAMINE® D-400 with 4,4 -bismaleimidouliphenylmethane (MDABMI):

The MDABMI (8.52g. 23.9 mmol) was dissolved in 45 ml chloroform at 40°C in a 250 ml 3-necked round-portioned flask under nitrogen. A solution of JEFFAMINE® D.400 (4.81g. 12.0 mmol) in 5 ml chloroform was added dropwise over a 5-10 minute period, resulting in a darkening of the solution. The chloroform was removed under vacuum, with the solution hoated in a hot water bath, leaving 12.5g of glassy orange solid.

### SPECIFIC EXAMPLE VI

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# Reaction of JEFFAMINE® ED-900 with MDABMI:

The MDABMI (6.00g. 16.8 mmol) was dissolved in 40 ml chloroform at 45°C. A solution of ED-000 (7.52g, 8.35 mmol) in 5 ml chloroform was added dropwise over a 5-10 minute period; the resulting orange solution was stirred at 40-45°C for two hours, then concentrated under vacuum (heating with hot water bath) to 12.0g of a very viscous grange liquid.

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#### SPECIFIC EXAMPLE VII

# 40 Reaction of JEFFAMINE® EDR-148 (triethyleneglycol diamine) with MDABMI:

The MDABMI (8.00g, 22.3 mmol) was dissolved in 50 ml chloroform and healed to 40° C The EDR-148 (1.65g, 11.1 mmol) was dissolved in 8 ml chloroform and added dropwise over a 10-15 minute period. The resulting solution was stirred at 40° C for two hours, then filtered from a small amount of solid and concentrated under vacuum to a yellow glass that softened at approximately 90-105° C.

## SPECIFIC EXAMPLE VIII

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# Homopolymerization of JEFFAMINE® D-400/MDABMI adduct:

A 1.5g sample of the glass was heated to 200°C over a 45 min period and held at that temperature for 35 min. The product was a hard, opaque red polymer with a decomposition temperature not yet determined.

# SPECIFIC EXAMPLE IX

Copolymerization of JEFFAMINE® ED-600/MDABMI adduct with JEFFAMINE EDR-148/EDR-148 BMI adduct

A mixture of 11.3g of ED-600 adduct and 3.38g of EDR-148/EDR-148 bismaleimide adduct was hoated under vacuum at 65°C for two hours and then poured into a 7" x 3.25" x 0.125" mold. The mold was heated in an oven at 160-170°C for 2.75 hr, and the product polymer was obtained as a red, semitransparent plaque with some voids resulting from evolution of volatiles. No properties have been determined

### SPECIFIC EXAMPLES XXXII

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Small samples of some of the polymers were prepared from these materials by hooting the prepolymers in a rectangular mold in air at 170° C 185° C A brief description of their properties is given in the table below. Amine(s) refers to the amine reacted with the BMI source (Michael acceptor).

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Example	eminə(s)	BMI source	properties
X	D-2000	MDA	red, flexible, Inelactic
l XI	T-6000	EDR-148	orange, flexible, elastic
XII	D-400	EDR-148	red, flexible, inclustic
XIII	ED-900	EDR-148	brown, flexible, slightly elastic
ΧIV	T-403	EDR-148	red, comewhat flexible, inelastic
XV	D-100	BAEE	red, flexible, inelastic
XVI	T-5000	MDA/BAEE	clear, yellow, clastic
XVII	D-400/T-403	EDH-148	clear, red, flexible
XVIII	ED-2001	EDR-148	orange, translucent, rather flexible, irielastic
XIX	EDR-148/D-4000	EDR-148	brown, apaque, very flexible and cleatic
l xx	EDR-148/T-5000	EDR-148	brown, upaque, flexible and strong
xxi	ET-3000	EDR-148	transparent, flexible, clastic
XXII	D-330	EDR-148	red, translucent, somewhat flexible, inelastic

Amines and BMI sources beginning with D-, T-, ED-, EDR-, or ET- refer to the JEFFAMINE amine products designated as shown. BAEE is bis(aminoethyl)ether and MDA is 4,4-methylone digniline. In Example XVI the molar ratio of MDA to BAEE is 1:1.

### Claims

 A bismaleimide derivative characterised in that it has the formula A or B and that it is formed at a temperature sufficient to cause thermal reaction between heated components of the mixture of:
 (a) at least one diamine of the formula

H2NCH2GH2-(-OCH2CH2-)n-NH2

wherein n equals 2, 3 or 4 and

(b) maleic anhydride

wherein components (a) and (b) form a bismaleamic acid represented by the formula

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which is further reacted with acetic annydride to form a bismaleimide of the formula A:

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wherein n = 2, 3 or 4, which optionally can be further reacted with a polyoxyalkyleneamine with a molecular weight greater than about 200 resulting in a bismaleimide derivative of a higher molecular weight polyoxyalkyleneamine of formula B:

wherein R1 and R2 are independently alkyl or hydrogen, x, y and z depend on the amine used, n is 1, 2, or 3, and m is predominantly 1.

2. A derivative according to claim 1 characterised in that the diamine component is selected from diethylene glycol diamine, triethylene glycol diamine, bisaminocthyl ether, JEFFAMINE® EDR-148 and JEFFAMINE® EDR-192.

3. A bismaleimide derivative according to claim 1 characterised in that it has the formula:

wherein n = 1, 2 or 3, with bisaminoethyl other as the diamine reactant for n = 1, with JEFFAMINF® EDR-140 as the diamine reactant for n = 2, and with JEFFAMINF® EDR-192 as the diamine reactant for n = 3.

4. A copolymer wherein one polymer comprises a bismalelmide compound of the formula-

wherein in equals 2, 3 or 4 and wherein the copolymer comprises a compound selected from the group consisting of aliphatic or aromatic diamines and unsaturated compounds.

5. A method of preparing a bismaleimide derivative characterised in that it comprises reacting a polyoxyalkyleneamine in a chlorotorm solution with an aromatic bismaleimide in a chlorotorm solution, optionally heating the solution and subjecting the solution to a vacuum to recover the aromatic bismaleimide product.

- R. A method according to claim 5 characterised in that the polyoxyalkyleneamine is of the formula H<sub>2</sub>N-(-CHR¹CH<sub>2</sub>O-),-(-CHR²CH<sub>2</sub>O-),-(-CHR²CH<sub>2</sub>O-)<sub>x-1</sub>-CH<sub>2</sub>CHR¹NH<sub>2</sub>
- where R1 and R2 are independently, alkyl or hydrogen, and x, y, and z depend on the amine used.
- 7. A method according to claim 5 characterised in that the polyoxyalkyleneamine is of the formula: NH<sub>2</sub>CH(CH<sub>3</sub>)CH<sub>2</sub>-[OCH<sub>2</sub>CH(CH<sub>3</sub>)]. NH<sub>2</sub>.

NH3CH(CH3)CHE-{OCH(CH3)CH2]x

Of

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HaN-CH2CH2(OCH2CIb)n-NH2

where n = 1 or 2.

- 6. A method according to any or claims 5 to 7 characterised in that the aromatic bismale/mide is 4,4'-bismale/midediphenylmethane.
- 9. A method according to any of claims 5 to 8 characterized in that the solution is heated at a temperature of from 50 °C-125 °C.
- 10. A method for preparing a liquid bismaleimideospartimide prepolymer from the solid bismaleimide of the formula:

- characterised in that it comprises reacting said sulid bismaleimide with triethylene glycol diamino at a temperature of from 0 °C to 125 °C to form a liquid prepolymer sultable for polymerization.
  - 11. A liquid bicmaloimidoaspartimide prepolymer characterised in that it comprises 60 to 90 weight percent bismaleimide of the formula:

wherein n = 2, 3 or 4, and 10 to 40 weight percent triethylene glycol diamine.

12. A novel aromatic bismaleimide derivative characterised in that it has the formula:

wherein  $R^1$  and  $R^2$  are independently alkyl or hydrogen,  $x_i$  y, and z depend on the amine used, and m is predominantly 1.

13. Any homopolymer or connolymer characterised in that it is formed by using the bismaleimide of claim 12.